5.111 Principles of Chemical Science

Fall 2008

Transition Metals and Coordination Complexes

See pages 2 and 3 of lecture 27 notes for an introduction to coordination complexes.
See page 5 of lecture 27 notes for a discussion of geometric isomers.

Chelate Effect in Coordination Complexes:

Ligands that bind a metal at one site are called unidentate or monodentate (one tooth).

Ligands that have two or more points of attachment to the metal are called chelating ligands and the coordination complexes are called chelates (greek for claws).

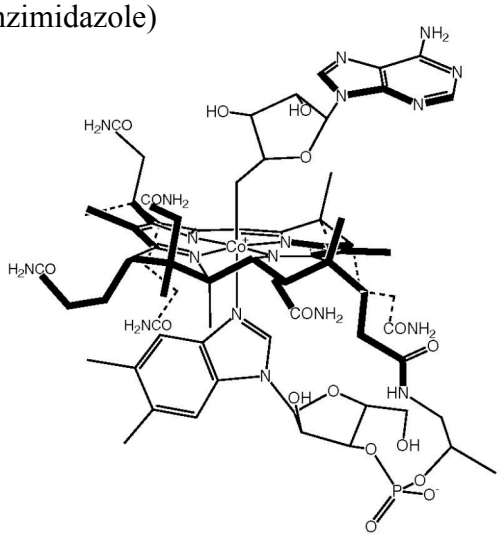
Bidentate – two points of attachment
Tridentate – three points of attachment
Tetradentate – four points of attachment (ex. corrin ring of vitamin B_{12})
Hexadentate – six points of attachment (ex. EDTA)

Metal chelates are unusually stable. This is partly due to the favorable entropic factor accompanying release of non-chelating ligands (usually H_2O) from the coordination sphere.

Examples from page 4 of Lecture 27 notes: Chelation Complexes in Biology

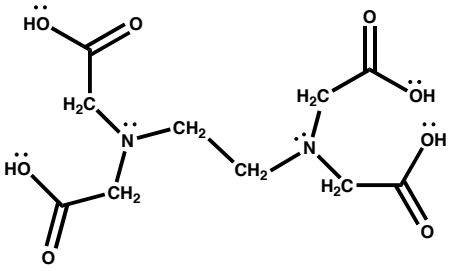
Vitamin B_{12}

In vitamin B_{12}, the cobalt is coordinated by a planar tetradentate ligand (corrin ring system). It is also coordinated by an upper axial ligand (5'deoxyadenosine) and a lower axial ligand (dimethylbenzimidazole)

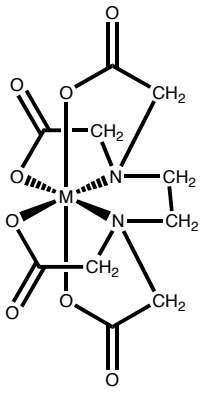


Dorothy Crowfoot Hodgkin used X-ray crystallography to determine the structure of vitamin B_{12}, for which she was awarded the 1964 Nobel Prize in Chemistry. Her work pioneered the use of crystallography to solve the structure of complex molecules. Today crystallography is used to determine structures of incredibly large and complex molecules, such as proteins.

Ethylenediamine tetraacetic acid (EDTA) and the treatment of acute lead poisoning

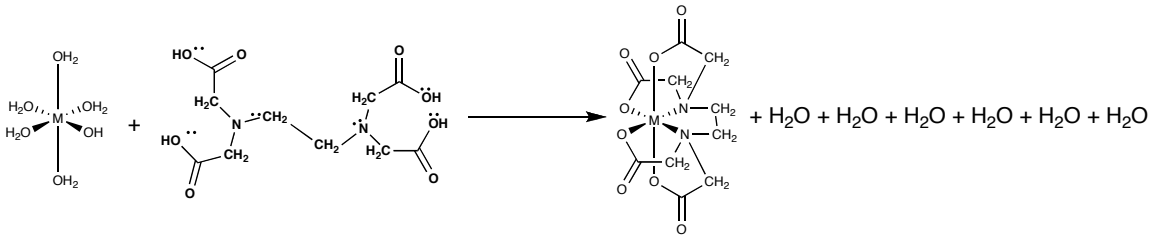


Free EDTA



EDTA in complex with metal (M)

Binding of EDTA is **entropically** favorable for a metal. Six molecules of H_2O are released for every 1 molecule of EDTA bound.



In medicine – ETDA is used as a treatment for acute lead poisoning.
EDTA chelates the lead, and the chelation complex is excreted from the body. This treatment is only used for severe cases of lead poisoning, and patienta are carefully monitored because EDTA also chelates other (essential) metals in the body.

<u>Other uses of EDTA include:</u>
Food additive – "added for freshness" since bacteria requires metals for survival
Bathtub cleaner – EDTA chelates Ca^{2+} in tub scum
Hollywood – In the vampire movie "Blade", ETDA is used to kill vampires by chelating iron in the blood.

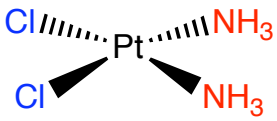
For a brief historical perspective on lead poisoning, see:
http://www.rsc.org/Education/EiC/issues/2006Sept/SoundbiteMolecules.asp

Geometric (Cis-Trans) Isomers

Stereoisomers:
Molecules with the same molecular formula and atomic connectivity, but different atomic arrangements in space. Geometric isomers can have vastly different properties.

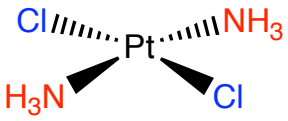
Example from page 5 of Lecture 27 notes: The Anti-Cancer Drug *Cis*-Platin

$[Pt(NH_3)_2Cl_2]$ has two geometric isomers. The *cis* isomer, *cis*-platin, is a potent chemotherapeutic agent, while the *trans* stereoisomer has negligible anti-cancer activity.



***cis*-platin**

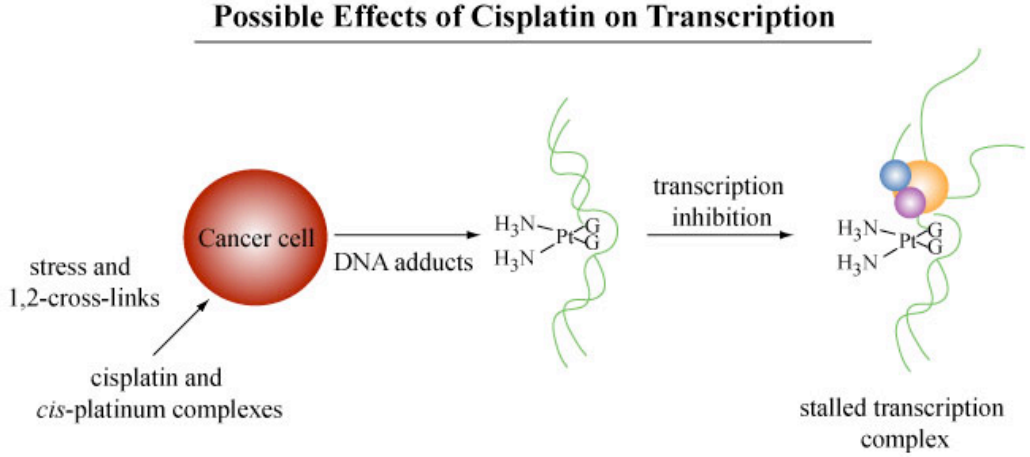
potent anti-cancer drug



***trans*-platin**

negligible anti-cancer activity (and toxic)

Putative mechanism of action: Following displacement of a chloride (Cl) ligand with water, ***cis*-platin** coordinates to DNA in cancer cells, thereby inhibiting DNA transcription and leading to apoptosis (programmed cell death). ***Trans*-platin** is thought to be deactiviated in cells and does **not** bind DNA.



The stalled transcription complex initiatesubiquitination and proteolysis of RNA Polymerase II, activating apoptosis.

Image by MIT OpenCourseWare.